THE EFFECT OF O_2 OXIDATION VERSUS WEATHERING IN AIR ON THE STRUCTURE OF THE APCS COAL SAMPLES DETERMINED BY THE EPR SPIN PROBE METHOD

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ABSTRACT

Eight vacuum dried Argonne Premium Coal Samples (APCS) were oxidized in a pure oxygen enclosed, moisture free environment, and the effects of oxidation alone on coal structure were studied by the intercalation of EPR spin probes [3-carboxy-2,2,5,5-tetramethylpiperidine-1-oxyl (VI), TEMPAMINE (VII) and TEMPO(VIII)]. These studies clearly differentiated between the effect of oxidation and the effect of moisture removal or addition on the physical and chemical structure of coals. The data shows a factor of 5 increase in spin probe retention for some coals oxidized in O_2 versus air, suggesting a large increase in oxidized material.

INTRODUCTION

Exposure to air during the weathering process has been previously shown to greatly alter the molecular accessibility of EPR spin probes in coal.[1] Weathered coals are subject to a loss of water and oxidation, both of which have been shown to have a strong effect on coal conversion,[2,3] and the physical and chemical structure of coal.[1] The effect of vacuum drying is also discussed elsewhere.[4] This technique has been very useful in studying molecular accessibility in coal samples.[5-7] Use of spin probes has been shown particularly advantageous when the spin probes contain polar substituents. Lignite and subbituminous coal contain carboxyl and hydroxyl groups. Nitrogen functionalities make only minor contributions in coal due to the low nitrogen content in coal. A spin probe with an amino substituent is a strong hydrogen bond acceptor, capable of only weak hydrogen bond donation. A spin probe with a carboxyl group is a strong hydrogen bond donor, but is only capable of acting as an acceptor through the carbonyl group. Thus these spin probes can interact and detect the presence of hydroxyl and carbonyl groups present in the coal matrix. The effect of size incorporation in the coal matrix can be determined by comparing a spin probe without a substituent (substituted only with a proton) to those similar in size containing a substituent. Solvents like pyridine are capable of hydrogen bonding with coal. Pyridine has been shown to break up the hydrogen bonding cross-links in the coal structure.[6] It is possible to displace hydrogen bonded spin probes with pyridine. It has been shown that the hydrogen bond donating ability increases in the series -H << -OH < -COOH < $-NH_2$.This feature is used to deduce the effect of oxidation on coal. It is the goal of this paper to use this technique to investigate the contribution of oxidation on the swelling properties of coal during the weathering process.

EXPERIMENTAL

Vials containing the APCS coals (defined previously[8]) were opened in a moisture free, pure Argon environment. The coals were vacuum dried in a vacuum desiccator for 18 hours. After being weighed, the coals were split into several aliquots. Five of these aliquots for each coal were placed under a dry, pure oxygen (99.9995%) environment. The remaining aliquot of each coal was then swelled in a spin probe solution. The samples undergoing oxidation were agitated each day to insure thorough exposure. Samples were taken at 4, 8, 15, 36 and 64 days of oxidation and swelled in a spin probe solution of toluene or pyridine. The swelling solvent was removed and the spin probe retention was measured by EPR. The three spin probes used in this study are shown in Figure 1. The previously published numbering system[1,5-7] has been used.

A detailed description of the experimental method for the intercalation of spin probes using swelling solvents has been previously published.[5-7] Briefly, 30 mg of a coal is swelled in toluene or pyridine under argon with 2 mL of 1 mM solutions of spin probes at about 298 K for 18 hours. The solvent is filtered off and the coal is vacuum-dried at room temperature for 2 hours. The coal is then washed in cyclohexane to remove any spin probes on the coal surface. This procedure also removes any spin probes from the macro or mesopores. The cyclohexane is then removed under vacuum. Finally, the coal is placed in a EPR tube and evacuated. The concentration of spin probes retained in the coal is then determined by EPR.

RESULTS AND DISCUSSION

The data is plotted three dimensionally for ease of analysis since so many samples were collected. The spin probe retention is expressed in terms of concentration in spins per gram versus the oxidation period in days and % carbon (dmmf) for each spin probe/swelling solvent combination. The coals were vacuum dried and put in a moisture free oxygen environment so that only the effects of oxidation on the coals could be studied. Due to the constraints of the limited available space for this paper, only the results for coals swelled in toluene with spin probe VI will be discussed. Spin probe VI was chosen because of its versatility in polar interactions.

Figure 2 represents the effects of oxidation on vacuum dried coals swelled in toluene with spin probe VI. The front edge parallel to the Days of Oxidation axis shows the transition that Beulah-Zap goes through during the oxidation process with respect to the polar spin probe VI. It is shown that Beulah-Zap undergoes by a structural collapse upon vacuum drying. Little change in retention is observed during the first eight days of oxidation. However, after eight days, a continued increase in retention of spin probe is observed until after 64 days a retention of 7.2 x 10^{18} spins per gram is observed. The structure must open during the oxidation process such that large amounts of spin probe VI are retained, because toluene is known to have little effect on breaking cross-links or other intramolecular interactions.[6]

Wyodak-Anderson, like Beulah-Zap, starts out with very little retention of spin probe VI and is not significantly affected by oxidation until 8 days of exposure to oxygen. At 8 days, the spin probe concentration increases to about 4 x 10^{18} spins per gram (shown in Figure 2 at point *f*). However, after the increase at 8 days, there is little change until 64 days of exposure where at point a sudden relative decrease in spin probe retention is observed. This would indicate a structural change where the spin probe was no longer able to access the coal structure, or a change in chemical structure which would limit the polar interactions between the coal structure and the spin probe.

Blind Canyon exhibits a decrease of spin probe retention after 8 days of exposure to oxygen (point d), followed by a steady increase in retention of spin probe VI until at 64 days of exposure to oxygen (point b), it retains nearly 1 x 10^{19} spins per gram, which is five times the amount retained in Blind Canyon coal weathered for 64 days, indicating a large increase in oxidized material.

The higher ranked coals, (Pittsburgh #8, Lewis Stockton, Upper Freeport and Poccahontas #3) which showed little change upon vacuum drying for coals swelled in toluene for spin probe VI, show significant changes in retention characteristics after just four to eight days of oxidation in oxygen (see area e in figure 2 or the expansion of Figure 2 given in Figure 3). For example, after 8 days of exposure to oxygen, Upper Freeport shows a retention of 3.7×10^{18} spins per gram. Initially, the spin probe retention was 1.1×10^{17} spins per gram while the highest retention observed for Upper Freeport coal weathered in air for 8 days was 4.5×10^{17} spins per gram. Both of these results are around an order of magnitude less than the results obtained for Upper Freeport oxidized in oxygen.

The effect of weathering vacuum dried coals in air and the effect of weathering fresh coals in air are presented in Figures 4 and 5A respectively for measurements of the retention of spin probe VI for 36 days. It is apparent that oxidation has a larger effect on molecular accessibility than vacuum drying during the weathering process (see previous paper).[4] However, the presence of water greatly affects oxidation of coals and alters the retention characteristics of most coals. It is noteworthy to compare the results of the oxidation of vacuum dries APCS coals in O_2 given in Figure 2 for 64 days with a similarly plotted curve (Figure 5B) for spin probe VI for fresh APCS coals weathered in air. By comparing Figures 2 and 5B, it can be seen that oxidation of coals for up to 64 days can result in a large increase in accessibility for polar spin probes into the coal structure, even for higher ranked coal.

CONCLUSION

Since it has been previously established[1] that Beulah-Zap undergoes a structural collapse, and no water is available to reopen the structure, it can be seen that oxidation can cause changes in the physical structure of low ranked coal. Medium ranked coal, especially Blind Canyon, exhibits a large increase in retention with exposure to oxygen, up to five times greater retention than coal weathered in air for similar periods. This suggests that medium ranked coal increases in oxidized material to a significant extent. Higher ranked coals, which do not exhibit large changes in accessibility upon vacuum drying or weathering, show large increases in retention of polar spin probes upon oxidation in oxygen. A comparison of 3 dimensional plots for vacuum dried coals oxidized in oxygen, vacuum dried coals weathered in air and fresh coals weathered in air shows that oxidation can have a large effect on the accessibility of polar spin probes in coal. By comparing features of these plots, it is possible to distinguish the effect of oxidation in the weathering process from water loss. Not shown or discussed are the results obtained for changing swelling solvents from toluene to pyridine, nor the effects of the change in spin probe functionality and the donor / acceptor properties of the constituents.

ACKNOWLEDGMENT

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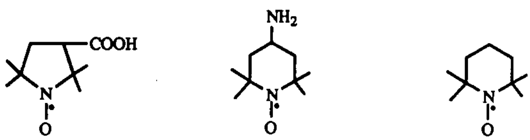

VI VII VIII

Figure 1. Spin probes VI, VII, and VIII

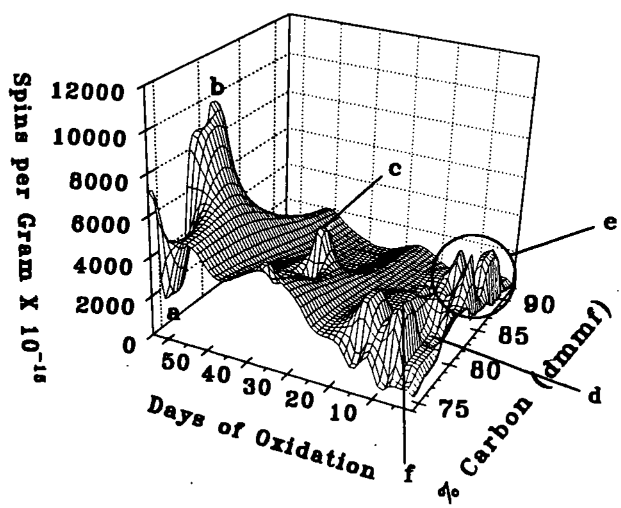

Figure 2. Retention of spin probe VI in O_2 oxidized, vacuum dried coal swelled in toluene expressed in spins per gram x 10^{-15} versus days of exposure to oxygen and % carbon (dmmf).

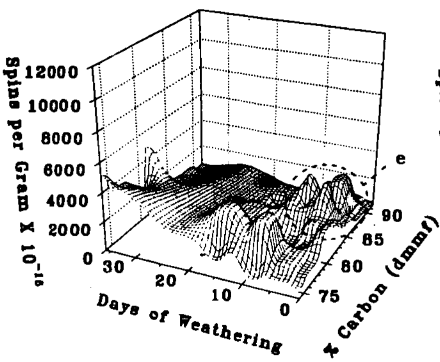

Figure 3
Retention of spin probe VI in vacuum dried coal swelled in toluene expressed as concentration in spins per grams x 10^{-15} versus days of exposure to oxygen and % carbon (dmmf). Expansion of Figure 2 for the first 36 days.

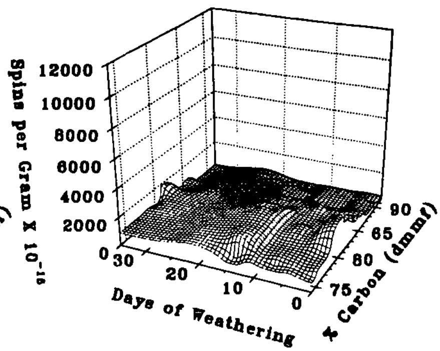

Figure 4
Spin probe VI retention in vaccum dried coal swelled in toluene in spins per gram x 10^{-15} vs. days of exposure to air and % carbon (dmmf) for up to 35 days.

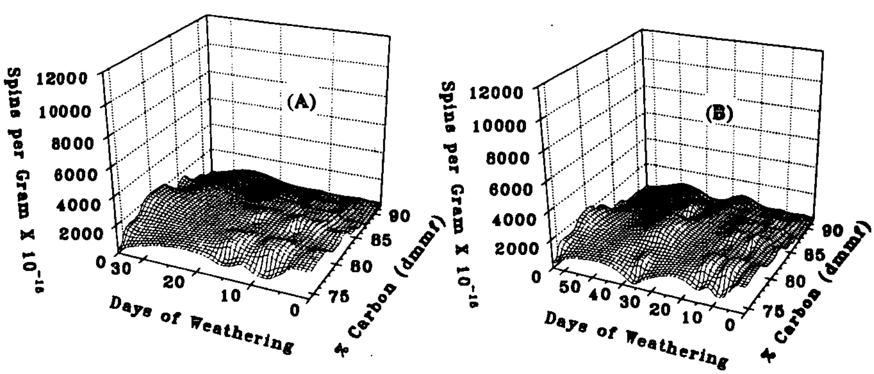

Figure 5. Retention of spin probe VI in weathered, fresh coal swelled in toluene expressed as concentration in spins per gram x 10^{-15} versus days of exposure to air and % carbon (dmmf) for up to: (A), 36 days and (B), 64 days.